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Published in:
International Journal of Mass Spectrometry

DOI:
[10.1016/S1387-3806\(99\)00266-3](https://doi.org/10.1016/S1387-3806(99)00266-3)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2000

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Citation for published version (APA):

Meijer, H. A. J., Neubert, R. E. M., & Visser, G. H. (2000). Cross contamination in dual inlet isotope ratio mass spectrometers. *International Journal of Mass Spectrometry*, 198(1-2), 45-61.
[https://doi.org/10.1016/S1387-3806\(99\)00266-3](https://doi.org/10.1016/S1387-3806(99)00266-3)

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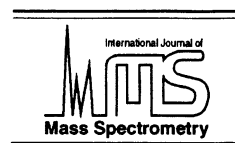
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International Journal of Mass Spectrometry 198 (2000) 45–61



Cross contamination in dual inlet isotope ratio mass spectrometers

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Received 20 October 1999; accepted 29 November 1999

Abstract

Since the early days of geochemical isotope ratio mass spectrometry there has always been the problem of cross contamination, i.e. the contamination of the sample gas with traces of reference gas (and vice versa) in a dual inlet system and the analyzer itself. This was attributable to valve leakages and could be corrected for. In modern leak-free machines this problem still influences the measurements by scale contraction. It limits the interlaboratory comparability to values unacceptable for, e.g. global carbon cycle investigations on atmospheric $\delta^{13}\text{C}$, with the need to integrate global datasets at a 0.01‰ precision level. No matter what the reason of apparent cross contamination (physical leakage, low pump efficiency, gas–wall interactions), we present a method to measure the actual cross contamination as well as algorithms to correct for it. By using isotopically enriched sample gas the effect on the reference gas is directly shown. Especially for biomedical applications, employing highly enriched materials, the nonlinear correction has to be applied. A long-time record of two machines shows the influence of vacuum breakage and the inlet system setup. We present a survey of cross contamination in some of the frequently used machines. The relatively poor raw results of two recent interlaboratory comparison experiments are explained in terms of cross contamination. Whereas the linear two-point normalization procedure considered by itself may be appropriate for some routine applications at natural isotope abundances, it always relies on relative δ values of two reference materials. There is an urgent need to establish absolute values for all scale-determining reference materials. We recommend the use of cross contamination measurements to at least determine the isotopic composition of all normalization materials as long as absolute measurements are not available. In principle, the cross contamination measurements should be used as a diagnostic tool on a regular basis. (Int J Mass Spectrom 198 (2000) 45–61) © 2000 Elsevier Science B.V.

Keywords: Gas isotope ratio mass spectrometry; Stable isotopes; Cross contamination; Normalization; Isotopic reference materials

1. Introduction

In the field of gas isotope ratio mass spectrometry (IRMS) the last decade has seen a new generation of commercial IRMS machines with improved stability and precision, as well as decreased amounts of sample

gas that is needed. The results of the stable isotope ratio measurements, e.g. for carbon, are usually expressed as the deviation of the isotope ratio of a sample from the ratio of a known reference material:

$$\delta^{13}\text{C} = ([^{13}\text{C}]/[^{12}\text{C}]_{\text{sample}}/[^{13}\text{C}]/[^{12}\text{C}]_{\text{reference}}) - 1 \quad (1)$$

and similarly for other isotopes. Since natural variations in isotope ratios are rather small, δ values are

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essentially small numbers, e.g. in the range of a few percent as for carbon. Therefore, they are usually expressed in per mill (‰). By using the new generation of IRMS instruments, the single-machine precision and repeatability improved enormously. As an example, it is currently possible to determine isotope ratios of $^{13}\text{C}/^{12}\text{C}$ in CO_2 gas with a precision and repeatability of better than 0.01‰. However, the interlaboratory accuracy hardly improved at all. Every time an intercomparison experiment (sometimes called ring test) is conducted—that is a series of reference materials (RMs) to be analyzed by several laboratories—the results show the same pattern: with reference materials that were in their isotopic composition close to the calibration materials, the interlaboratory accuracy was reasonably satisfactory—although still several times the intralaboratory precision. However, if the RM's isotopic composition differed from that of the calibration material by a considerable fraction of the natural range, interlaboratory differences grew to values that vastly exceeded the instrumental precision. A numerous amount of these ring tests have been conducted in the recent past, many of them under the guidance of the experts and consultants of the International Atomic Energy Agency (IAEA) isotope hydrology section (e.g. $\delta^2\text{H}$, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and $\delta^{34}\text{S}$ in a great variety of materials [1,2], $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of carbonates [3]; $\delta^{15}\text{N}$ of different materials [4], $\delta^{34}\text{S}$ of Ag_2S [5]). In the last three years, the ring test results for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of the so-called Global Network for Isotopes in Precipitation (GNIP) waters [6], $\delta^2\text{H}$ of pure hydrogen gases [7], and finally the National Institute of Standards and Technology (NIST) conducted ring test on $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of three pure CO_2 samples [8,9] all showed the same pattern. Though this is a dissatisfying state of affairs from a principal point of view, the isotope ratio community took rather pragmatistical measures to work around this lack of interlaboratory accuracy: several reference materials with their isotopic composition far from the primary calibration materials were attributed “consensus” isotope ratios with respect to the calibration materials. This was done by taking the mean value of the results of all laboratories taking part in the experiment, suppressing 3-sigma outliers. In the

case of $\delta^{18}\text{O}$ of water, a normalized scale was defined by using the calibration material Vienna Standard Mean Ocean Water (VSMOW) plus another water, isotopically depleted in the heavy isotopes [Standard Light Antarctic Precipitation (SLAP)], that was attributed a consensus mean value of $\delta^{18}\text{O} = -55.5\text{‰}$ with respect to VSMOW [10]. Of course the value attributed to this reference material is not necessarily absolutely correct, which implies that one per mill difference on this so-called normalized VSMOW-SLAP scale is most probably not really one per mill. However, normalizing helped to improve the intercomparability. Since the source of the interlaboratory inaccuracy has not been clear, it means that any step in the process between the original reference material (e.g. carbonate for $\delta^{13}\text{C}$, water for $\delta^{18}\text{O}$) and the final mass spectrometric analysis (on CO_2 gas for both examples) can be part of the cause. This forced the community to not only define reference materials for the measurement of each individual isotope, but also to provide at least intercomparison materials for every material that isotope ratio analyses are performed upon. For $\delta^{18}\text{O}$ this has led to the already mentioned VSMOW-SLAP scale for waters, but also to $\delta^{18}\text{O}$ reference materials with consensus values for carbonates and silicates. The idea behind this normalization is that every laboratory has its own laboratory-specific or even preparation- and mass spectrometer-specific scale-contraction or -expansion factor, disregarding the respective causes. By a two-point linear normalization across most of the natural range, this factor is removed. Evidence for this assumption follows again from those intercalibration exercises in which several RMs had to be determined. However, sometimes not much attention is paid to the fact that the scaling factors may vary significantly in time. This is not a short-coming of the normalization method and might be traced by regular measurements of the scale-determining material. The consequence of this normalization consensus is that the defined “consensus mean normalized δ scale” is a rather arbitrary one, it will no doubt not correspond to the “true” isotope ratios of the materials that are analyzed. Until now, only in the case of hydrogen in water it turned out to be possible to determine the absolute isotope ratios of

the calibration and reference materials, by using mixtures of isotopically nearly pure waters. By mimicking the VSMOW and SLAP waters in isotopic composition by using these mixtures, it could be determined in an absolute way that the $\delta^2\text{H}$ value of SLAP with respect to VSMOW is -428‰ . (De Wit et al. [11], revised value: $-427.8\text{‰} \pm 0.5\text{‰}$, Hagemann et al. [12]: $-428.5\text{‰} \pm 0.4\text{‰}$; Tse et al. [13] used the NMR technique and found $-428.8\text{‰} \pm 1.3\text{‰}$). Unfortunately, absolute measurements of other isotope ratios are not yet available with the requested accuracy. Laboratories working with artificially enhanced isotope ratios (such as for biomedical labeling) need additional, enriched reference materials, in order to “normalize” their measurements. Extrapolation of the linear normalization function used for the natural range usually fails for highly enriched samples (see Sec. 2.4 and Fig. 3), whereas cross contamination correction always considers nonlinearity in an appropriate way. Even though most laboratories manage to perform their research by using the concept of linear scale normalization, from a more basic point of view the situation is unsatisfactory. Therefore we have conducted research into the possible cause(s) of the scaling problems. We found that by far the main cause for the scaling problems is the “cross contamination” of sample and machine reference gases with each other in the mass spectrometer. This cross contamination is normally not caused by leaks, but rather by surface ad- and desorption effects in the inlet system and ion source of the IRMS machine, as investigated, e.g. by Gonfiantini et al. [14] on a time scale of several hours. The cross contamination effect always leads to scale contraction, but the amount appears to differ widely between the various machine types, and is dependent on specific measurement protocols and machine settings. The problem of cross contamination was noted earlier, in the beginning named and probably mainly caused by valve mixing [15], staying visibly disturbing with nonleaking valves but higher demands, e.g. [16,17]. However, it was not treated otherwise than by linear normalization or by scaling down the effects by means of a reference gas very similar to all samples. We have developed a measurement concept with which every laboratory is capable

of measuring the (nonlinear) scale contraction of every mass spectrometer and correct for it. At this point we want to emphasize that we are not dealing with sample-to-sample memory effects, where frequent use is made of enriched gases, but with sample-to-reference (and vice versa) contamination during one measurement in the mass spectrometer. Whereas the conventional memory thus is dependent on the differences in isotope ratios of two consecutive samples, the effect of cross contamination depends on the differences in isotope ratios between sample and reference gas. In a long series of sufficiently equally enriched samples, e.g. the conventional memory effect may become negligible for the later samples, whereas the cross contamination will stay equally important for all samples, as all samples are measured versus the same reference gas. Memory effects can be reduced or even excluded by pumping efficiently enough in the preparation and inlet systems, or by conditioning the systems with similar samples. The cross contamination can also be reduced to certain levels by extending the so-called idle times between the inlet to the analyzer and measurement of sample and reference gas, respectively. However, the dual inlet mass spectrometric isotope ratio measurement technique in principle includes the relatively fast change of sample, respectively, reference gas admittance to the ion source. The effect of cross contamination can be excluded (i.e. brought back to negligibility) only by using a reference working gas isotopically identical to the sample gas.

In the next section we explain our definition of cross contamination, and show how it can be measured. Then we show the cross contamination behavior for two of our IRMS machines through the time, for CO_2 and for hydrogen. We also indicate the corrections this cross contamination would give on natural samples and on enriched samples. In the latter case its nonlinear character becomes visible. In Sec. 3 we give a survey of typical cross contamination values for a few machine types presently on the market. Finally, we illustrate how the most recent hydrogen and CO_2 stable isotopes ring test results can be explained in terms of cross contamination, and we

give “best values” for the different gases, applying our concept of cross contamination correction.

2. Cross contamination in dual inlet isotope ratio mass spectrometers

2.1. Theory

Suppose we want to analyze a sample gas with isotope ratio r_s ($=[\text{minor}]/[\text{major}]$) on a dual inlet IRMS machine using a machine reference gas with isotope ratio r_r . Ideally, the measurement should give the true result of Eq. (1):

$$\delta_{\text{TRUE}} = \frac{r_s}{r_r} - 1 = \frac{r_s - r_r}{r_r} \quad (2)$$

Note, that for readability we always use the term “isotope ratios,” even if in fact isotopomere ratios are measured, e.g. $^{45}\text{CO}_2$ versus $^{44}\text{CO}_2$. As cross contamination affects the measurement of the ion beams $m/z = 45$ and $m/z = 44$, any cross contamination correction has to be applied on these isotopomere ratio measurements before the calculation of the final isotope ratio is done ($^{13}\text{C}/^{12}\text{C}$ in our example, considering the ^{17}O correction), according to the IAEA recommendations [18]. Note further, that “absolute ratios,” as we use this term here, means the measured ratio of the respective ion beams as given as the basic mass spectrometer output, corrected for background signals in an appropriate way. For all mass spectrometric work, but especially when dealing with enriched samples, the exclusion of sample-to-sample memory is a prerequisite.

Suppose now that, by whichever cause, a fraction η of the sample gas is admixed to the machine reference gas in the ion source during the measurement, and vice versa a fraction η of the machine reference gas contaminates the sample. The measured δ will then become

$$\delta_m = \frac{(1 - \eta)r_s + \eta r_r - (1 - \eta)r_r - \eta r_s}{(1 - \eta)r_r + \eta r_s} \quad (3)$$

The relation between the measured δ_m and the “wanted” δ_{TRUE} can be found from Eqs. (2) and (3) (as deduced in Appendix A):

$$\delta_{\text{TRUE}} = \frac{\delta_m}{1 - 2\eta - \eta\delta_m} \quad (4)$$

Eq. (4) shows that the correction indeed disappears if η becomes zero. The relation between δ_m and δ_{TRUE} contains a small constant correction term ($\eta \ll 1$) in the denominator, and even a term growing with δ_m , to correct for the nonlinear scale contraction that is caused by the cross contamination. However, as we will see later, the latter term only plays a significant role when measuring significantly enriched samples.

The causes of cross contamination can be three-fold.

- (1) Leaks in the IRMS between the sample and reference sides of the gas inlet system. The most obvious candidate is the so-called change-over valve that switches periodically between the admission of sample and reference gases to the ion source. Whereas older types of IRMSs usually had small leaks in the change-over valve (and even measuring protocols for determining them on a regular basis), the newer change-over valves, constructed out of four individual valves, are virtually leak-free.
- (2) The time between the change-over of the source admission from reference to sample gas and vice versa and the start of the data accumulation (the so-called idle time) is not long enough to get rid of all the rests of the previous gas in the source chamber, the analyzer and the connected tubing. Of course the cross contamination by this effect is dependent on the idle time, but also on the source geometry (dead volume), inlet flow and pump efficiency.
- (3) The adsorption and desorption processes that take place in the source. This term depends strongly on the source geometry, the materials used, and on the ion generation configuration and energy. Furthermore it depends on the “vacuum history” of the source, i.e. the time since the last venting and bakeout of the machine.

Instead of trying to characterize quantitatively each of these three sources of cross contamination individually, we present a measurement method for the total η , no matter which effect causes it.

2.2. Measurement of cross contamination

In order to be able to measure the difference between Eqs. (2) and (3) we have to make sure that, on the one hand, we are able to measure the true δ in some way, and on the other, perform a measurement where the effect of η is as large as possible. Furthermore, one should not be dependent on a material with a “given” or consensus δ value. We have found a scheme that fulfills these requirements, by comparing the measured absolute ratios of the ion beams on the reference side, when measuring first a highly enriched sample, and then the machine reference gas on the sample side, respectively.

Suppose we measure a highly enriched sample with isotope ratio r_{sE} against the machine reference gas with isotope ratio r_r . Including the cross contamination, the measurement of the absolute ratio of the sample gas will be (with indices m for measurements influenced by cross contamination and T for true; except for a set of machine-specific fractionation factors, that are of no importance here):

$$r_{sE}^m = (1 - \eta)r_{sE}^T + \eta r_r^T \quad (5)$$

and, similarly, on the reference side:

$$r_{rE}^m = (1 - \eta)r_r^T + \eta r_{sE}^T \quad (6)$$

On the other hand, if we measure the machine reference gas as sample gas “against itself,” the cross contamination is virtually absent, and we find for the absolute ratio:

$$r_r^m = r_r^T \quad (7)$$

As is shown in Appendix B, η can be calculated from measured quantities as follows:

$$\frac{\eta}{1 - \eta} = \frac{r_{rE}^m - r_r}{r_{sE}^m - r_r} \Rightarrow \quad (8a)$$

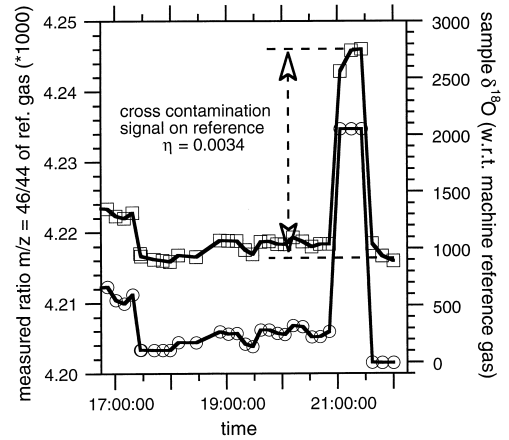


Fig. 1. Example of a daily course of absolute isotope ratios ($m/z = 46/44$) of reference gas (squares, left axis), as measured on our VG SIRA 9. Corresponding sample isotopic compositions (circles, lower line) are given as $\delta^{18}\text{O}$ as per mill w.r.t. reference gas on the right axis.

$$\eta = \left\{ 1 + \frac{r_{sE}^m - r_r}{r_{rE}^m - r_r} \right\}^{-1} \quad (8b)$$

Eq. (8) thus shows that a simple measuring protocol is sufficient for the measurement of the cross contamination in a specific machine on a specific time: One measures (usually two or three times) an enriched sample, and then, directly afterwards, the reference gas as a sample versus itself. Using the absolute ratios, Eq. (8) directly produces the cross contamination η . By using Eq. (4), all measurements of that specific day (or period) can be corrected. Fig. 1 shows a typical example of a part of a measurement day on our VG SIRA 9 instrument: the figure shows the $\{m/z = 46\}/\{m/z = 44\}$ ratio of the machine reference gas (left-hand scale), together with the ratio of the sample, as measured by the IRMS (right-hand scale, a δ scale is used for clarity). Clearly, the measured isotope ratio of the reference gas is proportionally influenced by the sample it is interchanged with: this is the directly visible cross contamination. During the specific day shown in Fig. 1, several enriched (biomedical) samples have been analyzed, and finally, at the end of the day our specific cross contamination measurements by using highly enriched gas have been performed. By using Eq. (8) this

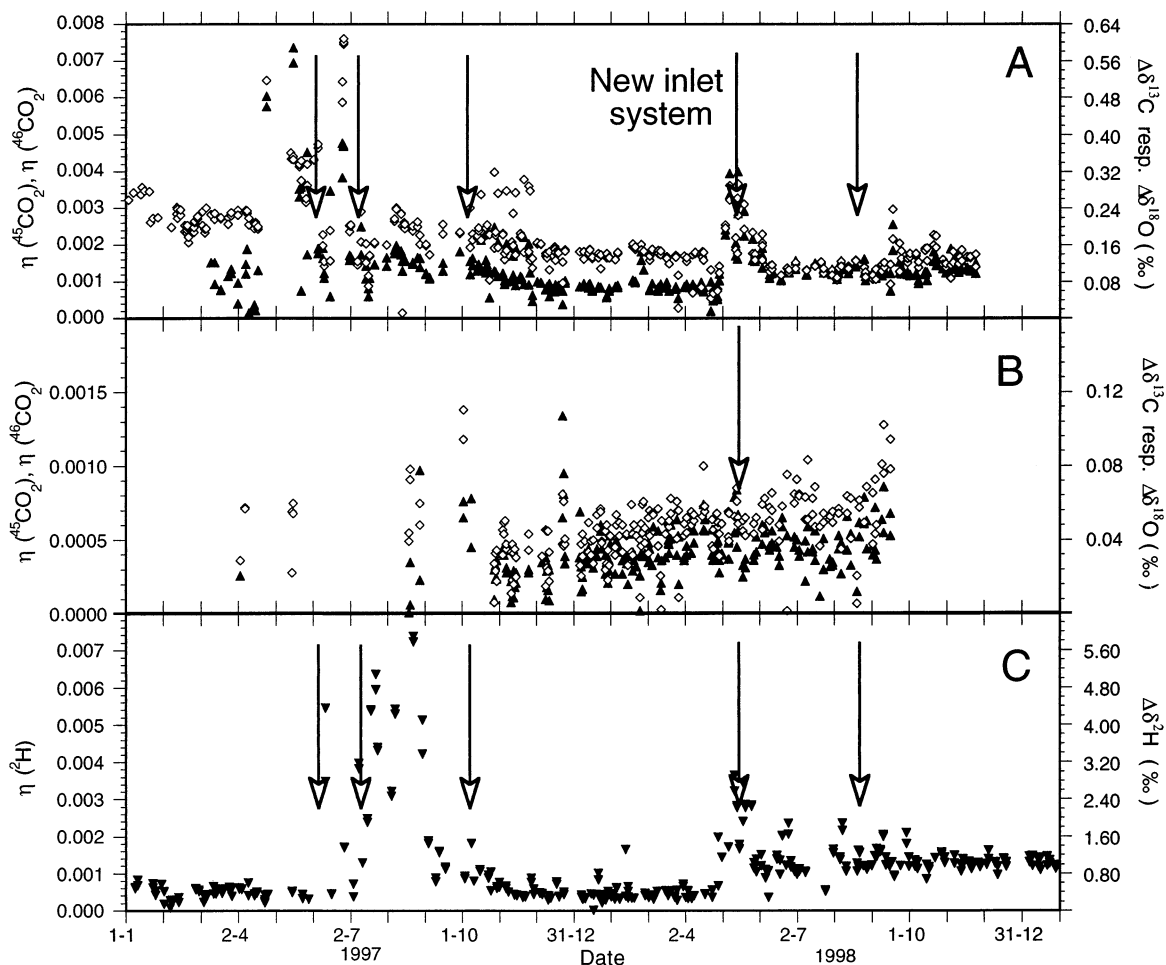


Fig. 2. Results of two years of cross contamination measurements on our VG SIRA 9: Panel A for $\delta^{45}\text{CO}_2$ (triangles) and $\delta^{46}\text{CO}_2$ (diamonds), panel C for $\delta^2\text{H}$; and on the MM 903: panel B for $\delta^{45}\text{CO}_2$ (triangles) and $\delta^{46}\text{CO}_2$ (diamonds). Times of vacuum-breakdown are indicated by arrows. The right scales show the respective influence in per mill at an isotopic difference between sample and reference of 40‰ for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, and of 400‰ for $\delta^2\text{H}$.

specific example produces a cross contamination of 0.0034. Such a cross contamination leads to a considerable scale contraction: over the natural $\delta^{18}\text{O}$ range for water, e.g. being about 50‰, this would already make a difference of 0.34‰.

2.3. Results of cross contamination measurements

We have measured the cross contamination of our two dual inlet machines—VG SIRA 9 and MM 903—routinely for over two years now, both for CO_2

and for hydrogen. Fig. 2 shows the results for parts of this period, for $\delta^{45}\text{CO}_2$ and $\delta^{46}\text{CO}_2$ for the VG SIRA 9 (A), for the MM 903 (B), and for $\delta^2\text{H}$ on the VG SIRA 9 (C). Some remarkable features are visible.

- (1) The η for hydrogen on the VG SIRA 9 (C) is much lower than $\eta(^{45}\text{CO}_2)$ and $\eta(^{46}\text{CO}_2)$. It is, however, even more sensitive to vacuum breakdown.
- (2) During a long period, η for both $\delta^{45}\text{CO}_2$ and $\delta^{46}\text{CO}_2$ were stable for the VG SIRA 9 (A) $\eta(^{46}\text{CO}_2)$ being roughly twice as high as

$\eta(^{45}\text{CO}_2)$. Then, due to several unfortunate events, vacuum breakdown occurred on the position indicated by the arrows. After such an event (which always was followed by a machine bake-out) η appears to be very unstable indeed.

- (3) In April 1998 we reduced the dead volume in the VG SIRA 9 source entrance system between the change-over valve and the analyzers considerably. This caused (apart from the instability that apparently accompanies a vacuum breakdown-bakeout sequence) $\eta(^{46}\text{CO}_2)$ to become lower, and in fact getting almost equal to $\eta(^{45}\text{CO}_2)$.
- (4) The η for both $\delta^{45}\text{CO}_2$ and $\delta^{46}\text{CO}_2$ of the MM 903 (B) are much lower than those for the VG SIRA 9, and also much more stable. It even does not suffer from any disturbance after vacuum breakdown (indicated by the arrows).

We interpret the findings as follows: (1) shows that cross contamination is dominated (at least in our machine) by surface exchange effects. Any leak would have more severe effects for hydrogen than for CO_2 . However, the “sticky” polarizable CO_2 gas is more likely to actively interact with the surface materials than hydrogen, in accordance with our findings. The response of η to vacuum breakdown-bakeout events (2) must be caused by the fact that a cleaned (heated) surface has more potential sites for relatively fast adsorption–desorption processes. On the longer run, the surface gradually gets into an equilibrium state. The MM 903 system is much less sensitive to these processes (4), which, apart from different source materials, also can be connected with the fact that the MM 903 has a smaller analyzer volume and is exclusively used for CO_2 . The VG SIRA 9 inlet system is flushed with CO_2 and hydrogen, respectively, alternating normally on a day-to-day basis. This also relates to the capillaries and change-over valve, however there are two different analyzers for CO_2 and hydrogen, but both of them with one common high-vacuum pump. The difference between $\eta(^{45}\text{CO}_2)$ and $\eta(^{46}\text{CO}_2)$ that disappeared after the dead volume got reduced considerably (3), shows that at least in the old configuration part of the cross contamination was connected to actual gas

remains of the reference/sample gas in the inlet pipework, after the data collection on the sample/reference gas had begun. These remains no doubt show fractionation, and this must be the cause of the considerable difference between $\eta(^{45}\text{CO}_2)$ and $\eta(^{46}\text{CO}_2)$.

It is not intended to thoroughly investigate the causes of the cross contamination. What is important here is its magnitude, and its variability. On the right-hand side of the figures the cross contamination correction [cf. Eq. (4)] is indicated, that must be applied to samples that are 40‰ (CO_2) or 400‰ (hydrogen) off the machine reference gas. The corrections are considerable. Even more, the unstable cross contamination behavior of the VG SIRA 9 in several periods would, without the ability to measure and correct for η , have lead to a very unstable performance, that otherwise probably would have been interpreted as loss of calibration. Application of the cross contamination correction, as we have done it, makes it possible to produce reliable results even in the unstable periods, although unmistakingly with somewhat larger uncertainties.

2.4. Nonlinear character of the cross contamination

The term $(\eta\delta_m)$ in the denominator of Eq. (4) gives the η correction, in principle, a nonlinear character. However, for the natural range of hydrogen and CO_2 isotopes, the product $(\eta\delta_m)$ is fully negligible compared to unity. It becomes significant, however, as soon as enriched samples are being analyzed, where the isotope ratios are more than 3–4 times the natural abundance. We perform such measurements on a routine basis for our biomedical research, in which isotope labeling (^2H and ^{18}O in water) is used for energy expenditure measurements (the so-called doubly labeled water method). For calibration purposes, we have a series of water isotope standards available, ranging from natural abundance to 7-fold (as for ^{18}O) or even 50-fold (^2H) enrichment. These standards have been produced by gravimetric mixing of isotopically pure waters [19]. This means the δ values of these standards are known in an absolute way with high accuracy, especially so for the highly

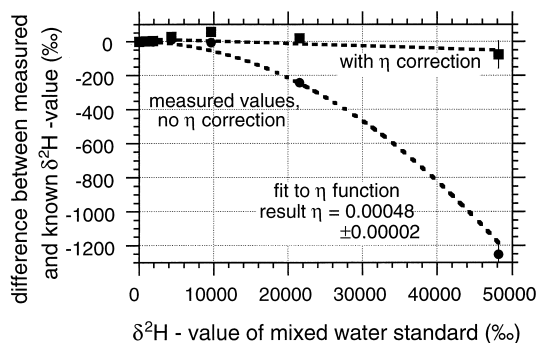


Fig. 3. The effect of cross contamination and its correction on highly enriched samples: the difference from the known value, given with and without cross contamination correction, the latter including a fit with Eq. (4).

enriched ones. However, measurement of these standards (without cross contamination correction) consistently gives deviations that increase in absolute and relative sense, with the degree of enrichment. Fig. 3 shows the results for hydrogen. On the x axis the known δ values of the samples are shown, whereas the y axis gives the difference between the known and the measured values (VG SIRA 9). Clearly, a nonlinear deviation is visible. However, if we apply the cross contamination correction, all corrected results lie within their uncertainties on the expected value. This can also be demonstrated by fitting the deviation between measured and known values by the cross contamination correction equation [Eq. (4)]. The dashed line shows a good fit, yielding an η of 0.00048, in accordance with the actually measured value of η for that specific period of time [early 1998, cf. Fig. 2(C)]. It is unnecessary to say that for this kind of samples the determination of, and correction with, the cross contamination is essential for reliable results.

3. Cross contamination in different IRMS machines

Whereas after this period of time, the cross contamination behaviour of our machines is well known and continuously monitored, the next question was what other machines and especially other types of

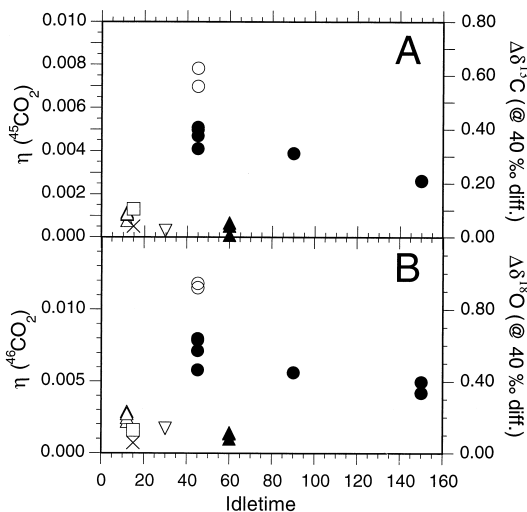


Fig. 4. Comparison of the cross contamination (left scale) in different types of dual inlet IRMS under their normal working conditions: panel A for $\delta^{13}\text{C}$, panel B for $\delta^{18}\text{O}$, as related to the idle times used. Circles refer to MAT 252 (old type), filled: normal conditions 16.5 nA ion current, open: current reduced by 35%, respectively, 50%. Closed triangles: MAT 252 (new type), VISC-window open, 13.3 nA. Open triangles: VG Optima (NIOZ, CIO). Squares: VG-SIRA. Crosses: MM903. The right scale shows the respective influence in per mill at an isotopic difference between sample and reference of 40‰.

machines would show. To get at least an idea of the magnitude of the η values, we have kindly requested several other groups (see acknowledgement section) to perform measurements with our natural abundance and enriched CO_2 standards. We were able to get results for the two machines with the highest market share at the moment, the Finnigan MAT 252 and the Micromass Optima. Fig. 4 shows the results for (A) $\delta^{13}\text{C}$ and for (B) $\delta^{18}\text{O}$. Although snap shots, the results are believed to be representative, as all machines were running in their respective routine mode without recent vacuum breakdown. Large variations of the MAT 252's performance with the idle time are known to the users [17,20]. The x axis in Fig. 4 shows the idle time that was used on the different machines. On the left-hand side, η is shown, whereas on the right-hand side the η correction on a 40‰ difference is shown (just as in Fig. 2). The numbers on that axis are alarming. Especially for the MAT 252 in "normal" use corrections of about 0.5‰ ($\delta^{13}\text{C}$) and 0.8‰

($\delta^{18}\text{O}$) are necessary. Note, that an idle time of 45 s is by far longer than applied by most of the users. Even more, variations in η with time as we observe them, would make the instrument de facto unusable for any high-precision work (when not using a reference gas very close to all samples). Recently, however, the MAT 252 design has been modified and now contains modified source parts, by using different materials. As can be seen in the figures, this reduces the cross contamination considerably. Note that the old-type MAT 252 was operated with the variable ion source conductance (VISC) window closed, whereas the new-type MAT 252 was run with the VISC window nearly open, the latter improving the pump effectivity by far. However, to date only a few of the machines have been upgraded. Still, none of all machines is really free of cross contamination. This means that the measurement of η and subsequent correction for it is necessary to produce a reliable scale for all IRMS machines. For hydrogen, unfortunately, measurements on other machine types are as yet not available.

4. Essay at a re-interpretation of recent ring tests

Recent ring tests, even if they were restricted to “high-quality” labs for the species in question, also suffered from a surprisingly poor interlaboratory reproducibility for materials that considerably differ in isotope ratio from the calibration material (but still in the natural range). Using our cross contamination concept, we reinterpret the latest two international ring tests, the ring test on three pure hydrogen gases [7], and the NIST ring test on three pure CO_2 reference materials [9], as good as this is possible with the measurements of the sample sets only (no enriched samples included).

4.1. NIST CO_2 ring test

To meet the need for pure CO_2 gas reference materials among the IRMS laboratories worldwide, NIST started a project where a large number of breakseals with CO_2 could be produced, all with

identical isotope ratios [8,9]. Three different RM gases have been produced, ranging from -4‰ to -41‰ with respect to (w.r.t.) VPDB for $\delta^{13}\text{C}$, and from -10‰ to -34‰ w.r.t. VPDB- CO_2 for $\delta^{18}\text{O}$. After many initial tests on reproducibility and purity, it was decided to organize a ring test with a restricted number of participants in 1997 [9]. In this ring test, three samples of each RM were provided. A total of 13 laboratories responded (one of them reported results of two different mass spectrometers, these are handled as different laboratories), and the results were presented at the latest IAEA expert meeting [21]. Care was taken not to introduce errors by different data processing for the conversion of $\delta^{45}\text{CO}_2$ and $\delta^{46}\text{CO}_2$ to $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. The reported data showed the already described effect: the spread in $\delta^{13}\text{C}$ varied from $\pm 0.08\text{‰}$ for the RM closest to the calibration material NBS-19 (having a defined $\delta^{13}\text{C} = +1.95\text{‰}$ w.r.t. VPDB), but $\pm 0.22\text{‰}$ for the RM with $\delta^{13}\text{C}$ around -41‰ VPDB. The situation for $\delta^{18}\text{O}$ was even worse, the standard deviation increased from $\pm 0.12\text{‰}$ for the RM with value -10‰ w.r.t. VPDB- CO_2 to $\pm 0.34\text{‰}$ for the RM with $\delta^{18}\text{O}$ around -34‰ w.r.t. VPDB- CO_2 . However, a laboratory's results behave in a systematic way: if a reported number is on the high side for one of the reference materials relatively close to 0, then this holds (with increasing deviations from the average) for the other RMs as well, and even in an analogous way for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. This can be expected when cross contamination is the main source of spread. Normalization in the conventional way, with concurrent measurements of CO_2 prepared from carbonate or water RMs, did improve the situation [9], but was not able to produce real favorable results. This was caused by the fact that not all laboratories reported carbonate or water RMs (and not all of them the same) and furthermore these carbonate and/or water RMs require a preparation step where errors can be introduced, as compared to pure CO_2 gas measurements. The normalized $\delta^{13}\text{C}$ values of RM 8563 of ten laboratories still showed a range from -41.06‰ to -41.59‰ .

If, as we assume, the varying contributions of cross contamination are the main cause of the spread, it should be possible to correct for this by fitting a

straight line to the deviation of each laboratory's measurement from the "assumed true" values. Preparation problems for the carbonate RMs, e.g. low quality (i.e. high water content) of the phosphoric acid, should show up as a constant offset here. But note that the primary calibration material NBS-19 calcite must be prepared under the same conditions. Since we deal with RMs within the natural range of isotope ratios, we can approximate Eq. (4):

$$\delta_{\text{TRUE}} \approx (1 + 2\eta)(\delta_m - \delta_{\text{CM}}) + \delta_{\text{CM}} \quad (9)$$

Here δ_{CM} is the δ value of the CO_2 produced from the calibration material NBS-19 at standard conditions (being +1.95‰ for $\delta^{13}\text{C}$ and -2.20‰ for $\delta^{18}\text{O}$) w.r.t. VPDB- CO_2 . In Eq. (9) we assume that all laboratories have related their working standards to NBS-19, either directly (for this ring test), or in a previous calibration effort. If we allow for an additional "calibration error" δ_{dev} the difference $\delta_{\text{TRUE}} - \delta_m$ will be equal to

$$\delta_{\text{TRUE}} - \delta_m = 2\eta(\delta_m - \delta_{\text{CM}}) + \delta_{\text{dev}} \quad (10)$$

Obviously, Eq. (10) is equivalent to a linear fit of the individual set of three differences (both for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) for each lab, the cross contamination η being expressed in the slope. Eventual systematic errors in the initial definition of δ_{TRUE} can be corrected to a certain extent in the fact that the average value for δ_{dev} will not be equal to zero.

Fig. 5 shows the results of these fits to the sets of three values for each of the 14 labs for $\delta^{13}\text{C}$ [Fig. 5(A)] and $\delta^{18}\text{O}$ [Fig. 5(B)]. The individual fit quality is highly satisfactory, giving evidence that cross contamination as we define it is indeed the main cause for the observed spread. Especially Fig. 5(B) shows that some of the participating labs have strong deviations in their calibration of NBS-19; however for most of the labs the combination of calibration deviation and cross contamination leads to relatively correct values in the region of δ values where most natural samples are positioned. Ten laboratories calibrated their working standards with NBS-19, however, small deviations from the standard conditions of the CO_2 preparation, which cancel out for the mea-

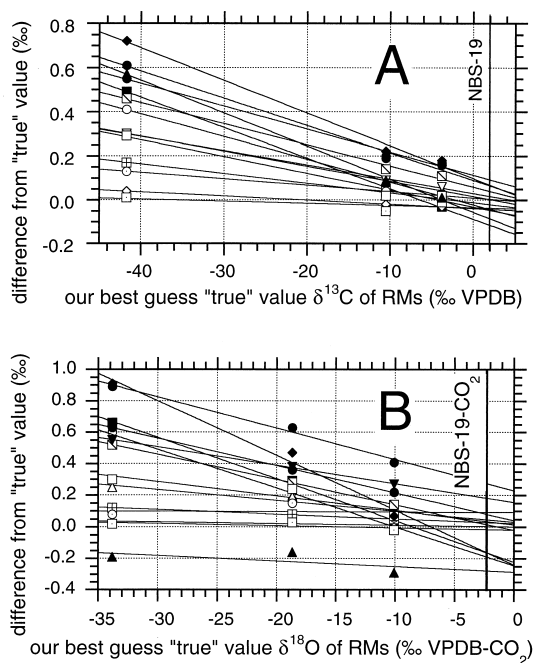


Fig. 5. Results of the NIST- CO_2 ring test (panel A for $\delta^{13}\text{C}$, panel B for $\delta^{18}\text{O}$) and linear fits for each laboratory's results.

surement of carbonates, might then show up as a "lab-specific VPBD scale" when measuring pure CO_2 . The other labs presumably do not calibrate their working standards with NBS-19- CO_2 itself, but they rather rely on values (possibly checked by other labs) of secondary reference materials that lie in their normal range of operation and consist of the respective material, e.g. CO_2 gas. Table 1 lists the cross contaminations computed and δ_{dev} , with their uncertainties, that follow from the fits in Fig. 5. All η values are well in the range we found in our machine survey above.

The results for η show that $\eta(^{18}\text{O})$ is generally bigger than $\eta(^{13}\text{C})$. For most of the labs with a significant cross contamination (except for no. 13, which is a clear outlier in this respect) the relation $\eta(^{18}\text{O}) \approx 2\eta(^{13}\text{C})$ holds. This corresponds to our findings as illustrated in Fig. 2(A), in the time before we reduced the dead volume in our inlet system. The phenomenon may be explained by fractionation during the evacuation of the inlet system, so that rem-

Table 1

Cross contaminations and offsets, as calculated for the CO₂ ring test participants' mass spectrometers

Laboratory	$\delta^{13}\text{C}$		$\delta^{18}\text{O}$	
	$\eta(\times 1000)$	$\delta_{\text{dev}} (\text{‰})$	$\eta (\times 1000)$	$\delta_{\text{dev}} (\text{‰})$
1	5.1 ± 0.4	-0.042 ± 0.019	12.3 ± 1.6	-0.19 ± 0.06
2	6.92 ± 0.16	-0.115 ± 0.009	13.2 ± 0.8	-0.16 ± 0.03
3	0.94 ± 0.03	-0.042 ± 0.002	0.5 ± 0.7	0.00 ± 0.03
4	3.41 ± 0.05	0.003 ± 0.003	3.4 ± 1.1	0.05 ± 0.05
5	2.19 ± 0.13	-0.020 ± 0.007	1.45 ± 0.11	0.029 ± 0.005
6	1.45 ± 0.007	0.004 ± 0.0004	0.1 ± 2.0	0.09 ± 0.08
7	4.8 ± 0.4	0.040 ± 0.022	8.00 ± 0.06	0.015 ± 0.002
8	3.23 ± 0.16	0.017 ± 0.009	5.9 ± 0.2	0.181 ± 0.009
9	0.5 ± 0.6	-0.04 ± 0.03	0.7 ± 0.8	-0.02 ± 0.04
10a	6.2 ± 0.7	0.065 ± 0.035	8.7 ± 0.2	0.08 ± 0.01
10b	5.2 ± 0.5	0.09 ± 0.03	9.9 ± 1.0	0.27 ± 0.05
11	3.8 ± 0.6	-0.05 ± 0.03	4.5 ± 2.1	0.04 ± 0.09
12	7.4 ± 0.7	0.07 ± 0.04	17.4 ± 2.3	-0.16 ± 0.10
13	7.5 ± 0.3	-0.085 ± 0.014	1.8 ± 2.2	-0.28 ± 0.09

nants of the gas are twice as much enriched in ^{18}O than in ^{13}C . However, since the phenomenon is apparently so widespread, it cannot be ruled out that surface exchange effects play a prominent role in this difference in η as well. Further, the effect of oxygen-atom (and thus isotopic) exchange with adsorbed water must be taken into consideration.

Whatever the exact cause(s), the cross contamination fit can now be used to individually correct the results for each lab (only for the found cross contamination, not for the—still more or less arbitrary— δ_{dev}). Fig. 6 shows the results after this correction [Fig. 6(A) for $\delta^{13}\text{C}$, Fig. 6(B) for $\delta^{18}\text{O}$]. Whereas comparing Fig. 6 to Fig. 5, the success of the cross contamination correction is obvious. It is also clear, that—in part because of the cross contamination compensation in the normal measuring range, discussed previously—some laboratories demonstrate considerable offsets; these can be treated as outliers in obtaining the final “best values” that are attained to the three reference materials. Table 2 gives these values, along with the standard deviation and the error in the mean. For $\delta^{13}\text{C}$, labs nos. 2, 10a and b, 12, and 13 are regarded as “outlier,” for $\delta^{18}\text{O}$ the same labs, except no. 10a, but also lab nos. 8 and 1 (cf. Table 1; the outliers are represented by filled symbols in Figs. 5 and 6). In Table 2 it is shown that the size of the errors is now independent of the deviation of the RM

from the calibration point. Further, the results are very precise indeed. If we would not recognize any lab as outlier, the errors in the mean would increase to

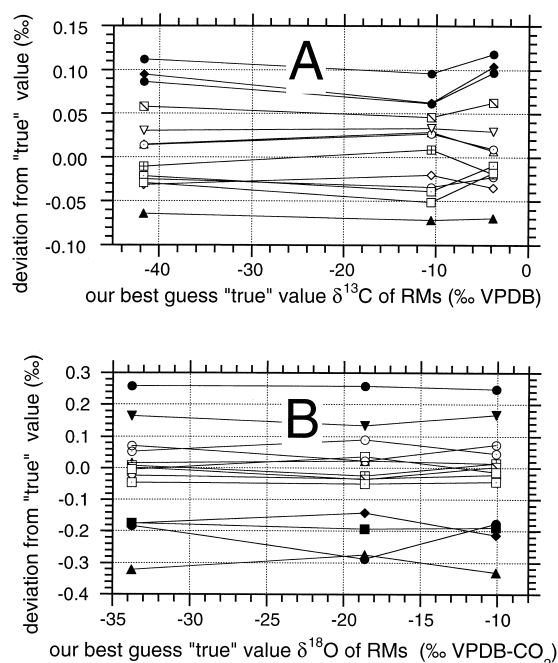


Fig. 6. Results of the NIST-CO₂ ring test and their reinterpretation with the cross contamination correction (panel A for $\delta^{13}\text{C}$, panel B for $\delta^{18}\text{O}$). Results shown with filled symbols were treated as outliers.

Table 2

The mean values and uncertainties of the CO₂ ring test RMs after cross contamination correction, the last two rows show the proposed values of Verkouteren [9]

RM	8562		8563		8564	
	$\delta^{13}\text{C}$ (‰)	$\delta^{18}\text{O}$ (‰)	$\delta^{13}\text{C}$ (‰)	$\delta^{18}\text{O}$ (‰)	$\delta^{13}\text{C}$ (‰)	$\delta^{18}\text{O}$ (‰)
Mean (this work)	−3.786	−18.610	−41.690	−33.760	−10.513	−10.058
Error in mean	0.010	0.018	0.010	0.014	0.012	0.014
Standard unc.	0.030	0.047	0.031	0.038	0.036	0.037
Verkouteren [9]	−3.76	−18.51	−41.56	−33.63	−10.45	−9.96
Verk. std. unc.	0.03	0.11	0.06	0.11	0.04	0.10

values around 0.016‰ for $\delta^{13}\text{C}$, and to 0.04‰ for $\delta^{18}\text{O}$. In Table 2 we also give the values proposed by Verkouteren [9] for the RM CO₂ gases. Especially the values of the isotopically depleted gases differ significantly. Though the values also were checked by self-consistent measurements of the ion beams $m/z = 44, 45, 46$, and 47 , and though our calculations are based on self-consistent linearity corrections only (apart from our own measurements), we still propose to have the intercomparison repeated, including cross contamination measurements done by all participants. Only by this means a real refinement of the “consensus mean” can be obtained, which is a prerequisite for a broad acceptance.

4.2. Hydrogen ring test

In 1995–1996 an extensive international hydrogen gas ring test was performed. Three pure hydrogen gases, with isotope ratios of $\delta^2\text{H} \approx$ (A) 0‰ (B), −400‰ and (C) −700‰ w.r.t. VSMOW were distributed to 38 laboratories worldwide. A total of 36 laboratories responded. Since no hydrogen pure gas scale is defined, results were expressed with respect to gas A. Part of the labs also produced numbers on the normalized VSMOW-SLAP scale, and gave results for their not normalized measurement of SLAP w.r.t. VSMOW as well.

The results of the tests showed similar features as the pure CO₂ tests discussed previously: there is a huge interlaboratory spread in the values of B w.r.t. A ($\pm 8.9\%$, 1σ) and C w.r.t. A ($\pm 15.3\%$, 1σ). The values reported for SLAP against VSMOW confirm the general picture. Furthermore, there is a good

correlation between the values that each individual laboratory produces for B, respectively, C w.r.t. A: if B is lower than average, then the same is true for C. The standard uncertainty of the deviation from the linear fit through all values of B w.r.t. A versus C w.r.t. A is only 0.8‰. This is essentially the same as the normalization Brand and Coplen [7] did, setting A to 0‰ and C at a fictive −700‰, finding a $1\text{-}\sigma$ standard uncertainty of 0.85‰ for the whole suite of 40 instruments involved.

This is an acceptable value for the intralaboratory reproducibility of $\delta^2\text{H}$ measurements. However, interpreting the results in terms of cross contamination is more complicated here than in the case of CO₂, since for $\delta^2\text{H}$ measurements also other corrections have to be applied. The most important one is the H_3^+ correction. Therefore, the reported scale can, in principle, also be expanded, and the simple rule that the most expanded scale is possibly about right, cannot be applied here. On the other hand, however, the $^2\text{H}/^1\text{H}$ ratio of the depleted reference material, SLAP, is known absolutely to be −428‰ w.r.t. VSMOW. Therefore, it would be logical to determine the cross contamination from the reported measured value of SLAP with respect to VSMOW. This solution again, however, is hindered in principal because the water to hydrogen conversion is notorious for fractionation effects, and in practice because only less than half of the participants of the ring test reported the gas measurements on their water-derived $\delta^2\text{H}$ scale. For the first reason, expressing the three pure hydrogen gases on the VSMOW-SLAP scale is not possible either. The ring test gave a mean value of $(-8 \pm 4)\%$ for A w.r.t. VSMOW ($N = 17$). Finally, the reported

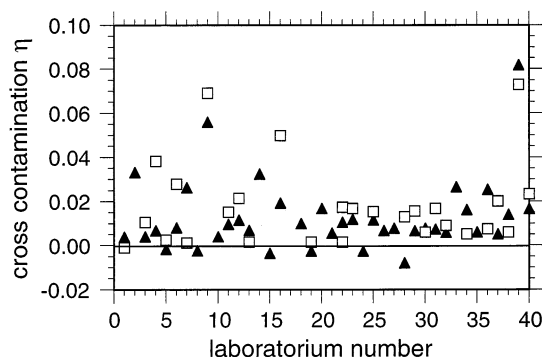


Fig. 7. Cross contamination η as calculated for the hydrogen ring test participants' mass spectrometers, derived from gas (triangles), respectively, VSMOW/SLAP (squares) measurements.

values for SLAP by the individual labs are not necessarily measured around the same time as the pure gases, since the ring test report only asked for "routinely obtained" values for SLAP.

A way to interpret the results of the ring test is to rely on our own measurements on the pure gases, that were cross contamination corrected, and that were properly corrected for the H_3^+ contribution, which is measured daily as well. The values thus obtained coincide with the "more expanded" scales, reported in the ring test. If we take these values for the assumed true ones, we can compute the cross contamination for each individual laboratory. The values we find are shown in Fig. 7, together with the cross contaminations that follow from the VSMOW and SLAP measurements (including preparation). The laboratory numbers are according to Brand and Coplen [7]. In the first place we observe that there is a considerable scatter between the results obtained from, respectively, pure H_2 and SLAP, with, however, a clear tendency that the SLAP-derived results are higher. This must be caused by additional fractionation effects in the conversion from water to hydrogen. In the second place, the cross contaminations are remarkably high. Although we have, contrary to the CO_2 situation, no cross contamination results for other machines than our own, we suspect that cross contamination by its own cannot account for these in part very high corrections. As mentioned before, other factors, most noticeably the H_3^+ correction, must play

a role, too. Our correction exercise resulted in the "best" values for the pure gases B and C with respect to A, being -412‰ and -705‰ , respectively, as compared to -410‰ and -705‰ , being our own results. The standard uncertainties for the individual values are 0.8‰ and 1.1‰ , respectively. The systematic uncertainty in these average values is no doubt at least that much. In order to more precisely determine the "pure hydrogen" scale, and separate cross contamination effects from other error sources, we suggest a new ring test to be organized. This ring test must include a much more detailed protocol (e.g. for the H_3^+ correction), as well as samples with ^2H -enriched hydrogen gas, for cross contamination determination.

For water samples, the situation is favorable since the isotopic composition of SLAP-hydrogen is known absolutely. Yet, laboratories should aim at obtaining a SLAP value that is as close to the "real" value as possible. If they have to apply a large correction factor due to machine settings, their results will no doubt be less accurate. The correction factor is most likely variable, and furthermore the assumed linearity of the correction might well be not completely true. Therefore it is favorable, also in the case of $\delta^2\text{H}$ measurements on water, to monitor and correct for cross contamination in the IRMS machine.

5. Discussion

The experience with our two dual inlet IRMS machines in the laboratory so far, the snapshot tests on other machines as well as the results of the reinterpretation of the pure CO_2 ring test (Sec. 4.1) lead us to the conclusion that, at least for CO_2 , cross contamination is by far the most important source of error in the accuracy of the δ -scale. Further, the here-described cross contamination measurement scheme is straightforward and it produces reliably precise results. However, the determination is not error-free, of course. The cross contamination may (and does) vary during the day, but it is only measured at the end of the day in our daily routine. This can be especially limiting in times when the IRMS is not stable, e.g. the first weeks after a venting-bakeout

event. Then, the precision of one measurement of η (a single inlet of the highly enriched gas, followed by natural abundance gas) is limited to typically $\pm 10\%$. The total precision can of course be improved by multiple inlets, but then gradually the cross contamination is influenced by the measurement procedure itself: the longer term adsorption/desorption processes will, in the case of multiple cross contamination measurements, leads to an average increase of the isotope ratio of the adsorbed CO_2 . This will, on this term, influence the detected absolute ratio of the machine working gas, even in the absence of enriched gas as sample. Therefore, in the end the measured cross contamination will be too low. In spite of our longer experience with the phenomenon, it is not easy to put an error bar on the correction. As a rule of thumb we state that the typical error in the correction is normally $\pm 5\%$, but considerably higher in times when we observe huge day-to-day variations in the cross contamination. If we consider the results presented in Sec. 4.1, we observe cross contamination corrections, for RM8563, ranging from almost 0 to almost 1‰. This means that, except for laboratories with extremely high cross contamination values, the expected error in the cross contamination correction, and therewith in the scale accuracy, is below 0.03‰. Of course, only an intercomparison between labs, that includes the cross contamination measurements, is able to give a more definite answer to the question of the accuracy limits.

In the case of H_2 , cross contamination is not the only effect that causes scale contraction; especially the H_3^+ correction can have significant influence, and can lead to scale contraction, but also to scale expansion. Therefore, correcting for cross contamination alone cannot guarantee an accurate δ -scale. The ring test discussed in Sec. 4.2 did not pay much attention (at least not in detail) to the H_3^+ correction, and therefore the (in part large) corrections that we have made to the data cannot be interpreted as pure cross contamination. In fact, our own experience with the cross contamination for hydrogen is that it is significantly lower than for CO_2 . On the other hand, the situation for hydrogen is clearer than for CO_2 , since the absolute ratio of SLAP is known to a satisfactory

accuracy. Therefore, using SLAP as RM for water measurements, and expanding (or contracting) the scale such that SLAP reproduces its known value is, in principle, a route that leads to an accurate $\delta^2\text{H}$ (water) scale. But, several remarks must be noted.

If the corrections that have to be applied are large and/or variable on a day-to-day basis, the accuracy of the procedure is limited by the error in the correction factor. This situation can occur if large (and/or variable) fractionation occurs in the transfer of water to hydrogen gas, or if samples are admixed with significant amounts of other water (either from the previous sample through memory effects, or from atmospheric water vapor).

The straightforward recipe to a better accuracy of the $\delta^2\text{H}$ scale includes, in our opinion, the cross contamination measurement as well as frequent H_3^+ correction measurements. By doing so, it can be guaranteed that the $\delta^2\text{H}$ scale for hydrogen gas on the IRMS machine is accurate, and that any deviations of SLAP from the known value must be due to one or more of the other effects mentioned previously.

At the University of Groningen there are four preparation lines for water-to-hydrogen conversion. All are based on water reduction by hot uranium, but the sample sizes, methods of sample introduction, glass surface areas (memory effects!) and hydrogen collection into sample flasks differ. By maintaining our IRMS $\delta^2\text{H}$ scale as accurately as possible, we have found that two of our systems now reproduce $\text{SLAP} = -428\text{‰}$ within the error bars. However, the other two systems in which we introduce the samples in glass capillaries (about 10 μL , for biomedical purposes) tend to deviate systematically by 1%–1.5% of the scale (from -422‰ to -424‰).

6. Conclusions

In the case of isotope ratio measurements on CO_2 , the most prominent cause of interlaboratory differences can indeed be described and corrected for by the concept of cross contamination. For hydrogen, cross contamination plays an important role as well, but probably does not dominate other causes of scale

variability, like especially the H_3^+ correction. Cross contamination always diminishes the measured difference between sample and machine working gas as compared to the true value: scale contraction occurs. For substances of which the δ values are far from the international calibration materials, deviations caused by cross contamination become substantial. For programs using isotope labelling, and consequently the analyses of highly enriched CO_2 or H_2 , cross contamination influences the results even in a nonlinear way. Only with the regular (probably daily) measurement of the cross contamination (and a frequent calibration check) it is possible to maintain a reliable, uncontracted “ δ scale,” by using only the calibration material. For laboratories that do not want to introduce highly enriched samples into their IRMS system, a way out would be to use a reference material in connection with the calibration material instead. This, however, provided, that the RM has been established by a group of laboratories which properly account for cross contamination. At present, the “consensus” values that are attributed to the various depleted reference materials that are kept by the IAEA Vienna and NIST Gaithersburg, are too high by a significant amount, since no laboratory that was involved in the ring tests did take cross contamination into account. Therefore it is highly recommended that a new ring test involving many of these reference materials will be organized, that includes measurement of and correction for cross contamination. Cross contamination measurement is also a valuable diagnostic tool. It can be used to optimize the IRMS performance, because it directly reproduces the results of varying pumping times and idle times on an easily detectable level. Further it clearly demonstrates the causes of instability after venting an IRMS, and improves the results of the IRMS especially in these periods.

Nothing is known up to now about cross contamination effects for other gases that are used in IRMS, such as N_2 , O_2 , and SO_2 . However, there are good reasons to believe that also for these gases cross contamination occurs, and that the measurement of and correction for it could improve the accuracy of interlaboratory comparisons significantly.

Acknowledgements

The authors gratefully acknowledge the help of their colleagues who contributed cross contamination measurements of their mass spectrometers: I. Levin (University of Heidelberg, MAT 252 old type), R.M. Verkouteren (NIST, MAT 252 new type), and R. Kloosterhuis (Netherlands Institute for Sea Research, Optima). P. Koeckhoven started an improved quality control assessment and the authors’ home-made Sample Information and Data Management system, the Isotech foundation friendly financially supported part of this research. The authors thank R.M. Verkouteren for fruitful discussions, access to his then unpublished dataset, and helpful comments on a first version of this manuscript.

Appendix A

In this appendix we deduce the relation between a measured δ -value δ_m , resulting from a measurement on a mass spectrometer with cross contamination η , and the true δ -value δ_{TRUE} [see Eq. (4)].

We want to measure a sample gas with isotope ratio r_s versus a reference gas with isotope ratio r_r . Ideally, δ_{TRUE} would be

$$\delta_{TRUE} = \frac{r_s}{r_r} - 1 = \frac{r_s - r_r}{r_r}$$

If a fraction η of sample gas is admixed to the reference gas and vice versa, we get a really measured δ -value δ_m of

$$\begin{aligned} \delta_m &= \frac{(1 - \eta)r_s + \eta r_r - (1 - \eta)r_r - \eta r_s}{(1 - \eta)r_r + \eta r_s} \\ &= \frac{(1 - 2\eta)(r_s - r_r)}{(1 - \eta)r_r + \eta r_s} \end{aligned}$$

So we find

$$\frac{1}{\delta_m} = \frac{(1 - \eta)r_r + \eta r_s}{(1 - 2\eta)(r_s - r_r)}$$

$$= \frac{r_r}{r_s - r_r} + \frac{\eta(r_s + r_r)}{(1 - 2\eta)(r_s - r_r)}$$

$$= \frac{1}{\delta_{\text{TRUE}}} + \frac{\eta}{(1 - 2\eta)} \frac{(r_s + r_r)}{(r_s - r_r)}$$

With the two following equations we can further transform our findings:

$$\frac{r_s}{r_s - r_r} = \frac{\delta_{\text{TRUE}} + 1}{\delta_{\text{TRUE}}} \quad \text{and} \quad \frac{r_r}{r_s - r_r} = \frac{1}{\delta_{\text{TRUE}}}$$

$$\frac{1}{\delta_m} = \frac{1}{\delta_{\text{TRUE}}} + \frac{\eta}{(1 - 2\eta)} \frac{1}{\delta_{\text{TRUE}}} + \frac{\eta}{(1 - 2\eta)} \frac{\delta_{\text{TRUE}} + 1}{\delta_{\text{TRUE}}}$$

$$= \frac{1}{(1 - 2\eta)} \left\{ \frac{1}{\delta_{\text{TRUE}}} + \eta \right\}$$

This converts directly into Eq. (4):

$$\delta_{\text{TRUE}} = \frac{\delta_m}{1 - 2\eta - \delta_m \eta}$$

Appendix B

To determine the cross contamination η , we make use of the measurements of the absolute isotope ratios $r = (\text{signal rare isotope})/(\text{signal most abundant isotope})$, which is in fact the ratio of the respective ion beam currents, commonly produced as the mass spectrometer's output. The indices r_r and r_s stand for the ratios of reference and sample gas, respectively. The second indices r_{rE}/r_{sE} and r_{rN}/r_{sN} indicate that the sample gas, being measured versus the machine reference gas, is isotopically enriched in the rare isotope (E) or has a natural isotope ratio (N), respectively.

Taking into account the cross contamination η , we look at the ratio of the difference between the absolute ratios of the reference gas when measuring an enriched respective natural sample, and the difference between the absolute ratios of the sample gas when measuring an enriched respective natural sample:

$$\frac{r_{rE}^m - r_{rN}^m}{r_{sE}^m - r_{sN}^m} = \frac{(1 - \eta)r_r^T + \eta r_{sE}^T - r_{rN}^m}{(1 - \eta)r_{sE}^T + \eta r_r^T - r_{sN}^m}$$

If we use the reference gas itself as a sample, this simplifies to

$$\frac{r_{rE}^m - r_{rN}^m}{r_{sE}^m - r_{sN}^m} = \frac{r_{rE}^m - r_r^T}{r_{sE}^m - r_r^T}$$

$$= \frac{(1 - \eta)r_r^T + \eta r_{sE}^T - r_r^T}{(1 - \eta)r_{sE}^T + \eta r_r^T - r_r^T}$$

$$= \frac{\eta(r_{sE}^T - r_r^T)}{(1 - \eta)(r_{sE}^T - r_r^T)}$$

$$= \frac{\eta}{1 - \eta}$$

So we can calculate the cross contamination η from the measurements of an isotopically enriched sample and of the reference gas versus the same reference gas:

$$\eta = \left\{ 1 + \frac{r_{sE}^m - r_r^T}{r_{rE}^m - r_r^T} \right\}^{-1}$$

By measuring the respective absolute values of the isotope ratios we determine η with the accuracy of a few percent, which is sufficient for the cross contamination correction. As our usual practice is to use gases enriched by thousands of per mill, it even would be a good approximation to use any gas in the range of natural isotope ratios instead of the reference gas as a sample.

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